Filtration of nanoparticles: evolution of cake-structure and pressure-drop

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Nanoparticle filtration

- Removal of wanted or unwanted particles
  - E.g. Flame-synthesized catalytic nanoparticles or diesel soot from engines

- Pressure-drop build-up is major parameter
  - Too high $\Delta P$ may halt or damage the engine [1]
  - Affects fuel economy
  - Highly related to structure of filter deposit (cake)

Setten et al., (2001), Catalysis Reviews, 43(4), 489-564
Cake formation

Filtration of nanoparticles

Highly porous cake : > 95 % [1,2]

Low penetration into substrate even for particles much smaller than the capillary

Analogous to thermophoretic deposition onto non-porous substrates

Structure determined by Pe [3,4]

Ballistic limit (85% porosity / 15 % solid volume fraction, $\phi_{sd}$) reached above Pe > 10

At Pe < 10, $\phi_{sd} = f(\text{Pe})$

$$Pe = \frac{d_p \cdot U}{2D}$$

$d_p$: Particle diameter
$U$: Approach velocity
$D$: Particle diffusion coefficient

Filtration regimes

Many models describe $\Delta P(t)$ [2-5]

Requires, however, knowledge of cake structure (solid volume fraction) and clogging time.

Our approach

Particle (spherical, monodisperse) tracking by Langevin dynamics

Deposition one-at-a-time [1]

Irreversible deposition

No deposition on surface between pores (≈ high porosity)

Results

Solid volume fraction profile

Clogging time, $t_{cl}$

Time until $F_{c,i} = 0$

Filtration efficiency $\eta(t)$

$\eta = 1 - F_{c,o}$

Pressure-drop $\Delta P(t)$

From $\phi_{sd}(z)$

$$\phi_{sd}(z) = \frac{V_p(z)}{V_{tot}}$$

$V_p(z)$: Total particle volume at position $z$

$F_{c,i}$: Fraction of flux entering capillary

Capillary

$F_{c,o}$: Fraction of flux exiting capillary
Structural evolution at Pe = 1

- **Capillary filtration**
- **Capillary clogging**
- **Cake growth**

Deposition focused near inlet of capillary

In agreement to experimental findings [1]

- \(d_p = 50 \text{ nm}\)
- \(C_0 = 10^{14} \text{ m}^{-3}\)
- \(2R_c = 4 \mu\text{m}\)

Solid volume fraction evolution

- Constant $\phi_{sd}$
- Cake
- Capillary

$\phi_{sd}$

- $1000\,s$
- $800\,s$
- $630\,s$
- $320\,s$
- $50\,s$
- $t = 10\,s$
- $t > 630\,s$

$z (\mu m)$

$Pe = 1$

$R_c = 2\,m$

$d_p = 50\,nm$
Onset of cake formation

$t_{cl}$ not linear with the particle flux ($\propto Pe$)

Due to increased packing

$\rightarrow$ Larger $\phi_{sd}$
Structures at $t_{cl}$ vs Pe

Increasing $\phi_{sd}$

A-A

Pe = 0.01  0.1  1  10

Void conical structure
Cake $\phi_{sd,c}$ and clogging time $t_{cl}$

$\phi_{sd,c}$ follows s-shaped curve

$$\phi_{sd,c} = 0.15 \left(1 + \frac{1.5}{Pe}\right)^{-0.5}$$

$t_{cl}$ seems to follow power-law with $Pe$


Estimation of clogging time

\[ t_{cl} = \frac{2R_c \phi_{sd,c}}{UC_0 v_p} \]

- \( R_c \): Capillary radius
- \( C_0 \): Aerosol concentration
- \( v_p \): Volume of single particle

Graph showing the relationship between clogging time and capillary ratio, with different markers for varying values of \( R_c/d_p \) (20, 40, 80). The correlation coefficient \( R^2 = 0.996 \) and range of Pe (Péclet number) from 0.01 to 10 is indicated.
Comparison to filtration theory

\[ \Delta P_{\text{cake}}(t) = P_0 - \sqrt{P_0^2 - \frac{2\mu U^2 P_0}{B_{0c}}} C_0 \nu_p (t - t_{cl}) \]

\[ B_{0c} = \frac{d_p^2}{150} \left( \frac{1 - \phi_{sd,c}}{\phi_{sd,c}^2} \right)^3 \]

\( d_p = 50 \text{ nm} \)

\( C_0 = 10^{14} \, \text{m}^{-3} \)
Conclusions

- Full transition between capillary and cake filtration studied by first principles
- Deposition focused near capillary inlet
- Capillary clogging followed by cake growth
  - Characterized by the clogging time $t_{cl}$
  - Constant solid volume fraction $\phi_{sd,c}$ function of $Pe$
  - Pressure-drop evolution in agreement with cake filtration theory
- Simple correlation derived between process parameters, clogging time and cake solid volume fraction

\[
\phi_{sd,c} = 0.15 \left( 1 + \frac{1.5}{Pe} \right)^{-0.5}
\]

\[
t_{cl} = \frac{2Rc \phi_{sd,c}}{UC \nu_p}
\]
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Functional nanoparticle films

Applications:

Membrane filters (Andersen et al., 2002)

Catalysis (Thybo et al., 2004)

Fuel cells (Chakraborty et al., 2005)

Gas sensors (Mädler et al., 2006a)


Solid volume fraction evolution at low Pe

Maximum $\phi_{sd}$

No preferential growth

Low Pe

$\phi_{sd, c}$

$z$ (\(\mu m\))
Two region pressure-drop model 1

Direction of flow

Open region

Deposited region

LD model

Cross-sectional view

Simplified model
Two region pressure-drop model 2

Slice dz
(top-down view)

LD model

Poiseuille’s law

Equi-pressure

Darcy’s law

Simplified model

Equi-pressure

dP/dz (dep.) = dP/dz (open)
Two region pressure-drop model 3

Compressible flow

\[ \Delta P = P_0 - \sqrt{P_0^2 - \frac{16Q_0 P_0 \mu}{\pi}} \int_0^{\delta(t)} dz \left\{ \frac{1}{8(R_c^2 - R_o(t, z)^2)B_0(t, z) + R_o(t, z)^4} \right\} \]

Valid both inside and outside capillary!

\( R_o = R_c \rightarrow \text{Poiseuille's law} \)

However, above the deposit, when \( R_o = R_c \) we set \( \frac{dP}{dz} = 0 \)

- \( R_o \): Radius of open region
- \( R_c \): Initial capillary radius
- \( \delta(t) \): thickness of deposit
- \( P_0 \): Inlet pressure (1 bar)
- \( Q_0 \): Flow at \( P_0 \)
- \( \mu \): Viscosity
- \( B_0(z) \): Darcy permeability
Two region pressure-drop model 4

Compressible flow (cont.)

At cake growth \((t > t_{cl}, \text{ clogging})\) \( R_0 \rightarrow 0 \)

\[
\Delta P = P_0 - \sqrt{P_0^2 - \frac{2Q_0 P_0 \mu}{\pi R_c^2} \int_0^{\delta(t)} \frac{dz}{B_0(t,z)}}
\]

\[
= P_0 - \sqrt{P_0^2 - \frac{2Q_0 P_0 \mu}{\pi R_c^2 B_{0c}}} \delta_{\text{cake}}(t) + \Delta P_{\text{clog}}
\]

Pressure-drop over cake (const \(\phi_{sd,c}\))

Same equation as in article

"Filtration theory"

\(B_{0c} : \text{ Darcy permeability in cake (constant)}\)
Two region pressure-drop model 5

Cake growth (cont.) : \( R_0 = 0 \) and \( \eta \rightarrow 1 \) (all particles filtered)

\[
\delta_{\text{cake}}(t) \pi R_c^2 \phi_{sd,c} = C_0 \nu_p Q_0 (t - t_{cl}) \quad \Rightarrow \quad \delta_{\text{cake}}(t) = \frac{C_0 \nu_p Q_0 (t - t_{cl})}{\pi R_c^2 \phi_{sd,c}}
\]

\[
\Delta P = P_0 - \sqrt{P_0^2 - \frac{2Q_0^2 \nu_p C_0 \nu_p \delta_{\text{cake}}(t)(t - t_{cl}) \Delta \rho_{\text{clog}}}{\pi R_c^2 B_{0c} \phi_{sd,c}}}
\]

Pressure-drop over cake (const \( \phi_{sd,c} \))

Pressure-drop in clog

\[\delta_{\text{cake}} \quad \text{Height of filtercake} \]

\[C_0 \quad \text{Aerosol concentration} \]

\[\nu_p \quad \text{Volume of 1 particle} \]

\[t_{cl} \quad \text{Clogging time} \]

**Incompressible flow**

\[
\Delta P = \frac{8Q_0 \mu}{\pi} \int_0^{\delta(t)} \frac{dz}{8(R_c^2 - R_o(t,z)^2)B_0(t,z) + R_o(t,z)^4}
\]
Pressure-drop model comparison 1

\[ \Delta P \]  
\[ Pe = 1 \]  
\[ d_p = 50 \text{ nm} \]  
\[ C_0 = 10^{14} \text{ m}^{-3} \]  
\[ R_c = 2 \mu m \]  

Average \( B_0 \) model overestimates \( \Delta P \) evolution

Only small difference after clogging \((t > t_{cl})\)
Pressure-drop model comparison 2

$R_o > 0$

t = $t_{cl}$
(2000 s)

$\Delta P$ after $t_{cl}$

Larger $\Delta P$

$\phi_{sd,clog}(z) = \frac{V_p(z)}{\pi(R_c^2 - R_o^2)\Delta z} > \phi_{sd}$, when $R_o > 0$

$Pe = 0.1$

$dp = 50$ nm

$C_0 = 10^{14}$ m$^{-3}$

$R_c = 2$ μm

Average Permeability Model

Two Region Model

Lower Permeability

$Ro > 0$
$\phi_{sd,c}$ : Influence of polydispersity
Agglomerate deposition
Deposited volume per particle:

\[
\frac{\Delta V}{\Delta N} = v_p = \frac{\pi (R_0(t) - R_0(t + \Delta t)^2) \cdot d_p \cdot \phi_{sd,c}}{\Delta N}
\]

Deposited particles per time:

\[
\frac{\Delta N}{\Delta t} = Q C_0 \cdot \frac{R_0 d_p}{R_c^2} \cdot \text{Fraction intercepted}
\]

Combined:

\[
\frac{\pi (R_0(t)^2 - R_0(t + \Delta t)^2) \cdot d_p \cdot \phi_{sd,c}}{\Delta t} = Q C_0 v_p \frac{R_0(t) d_p}{R_c^2}
\]

\[
\Delta t \to 0
\]

\[
\frac{2 R_c d R_0 \cdot \phi_{sd,c}}{d t} = \frac{Q}{\pi R_c^2} C_0 v_p \phi_p
\]

\[
d R_0 = \frac{U C_0 v_p}{2 \phi_{sd,c}} d t
\]
Langevin dynamics

Equation of motion

\[ m \ddot{v} = -f(v - w) + F + X \]

- \( m \)  Particle mass
- \( \dot{v} \)  Particle acceleration
- \( V \)  Particle velocity
- \( W \)  Fluid velocity
- \( F \)  External forces
- \( X \)  Brownian force

Friction coefficient \( f = \frac{3\pi \mu d_p}{C_c(d_p)} \)
Calculation of pressure-drop

Pressure drop in capillary:
  Hagen-Poiseulle equation

Pressure-drop in cake before clogging:
  Modified D’Arcy’s law

Pressure-drop in cake:
  D’Arcy’s law
Pressure drop in capillary

Basis: Hagen-Poiseuille

Assumptions - in a slice dz:

- Particle deposition decreases effective capillary size (Spurny et al., 1969; Fan and Gentry, 1978)
- Deposited layer << permeable than open part of capillary

\[
P \frac{dP}{dz} = -\frac{8 \mu U P_0}{(1 - \phi_{sd}(t,z))^2 R_c^2}
\]

- P : Pressure (Pa)
- z : Depth (m)
- U : Face velocity (m/s)
- P_0 : Inlet pressure (101325 Pa)
- R_c : Capillary radius (\(\mu\)m)
- \(\mu\) : Gas viscosity (kg/ms)
- \(\phi_{sd}(t,z)\) : Solid volume fraction of deposit at pos. ”z” and time ”t”.
Darcy permeability

Basis: Darcy’s law

Assumption - in a slice $dz$:

Application of an effective permeability

Effective pore size →

Effective permeability

(Jackson, 1977)

\[
B_0(t, z) = \frac{d_p^2}{72} \frac{(1 - \phi_{sd}(t, z))^3}{\phi_{sd}^2(t, z)}
\]

Particle size, $d_p$, Solid volume fraction, $\phi_{sd} →$

Effective pore size, $D_c$, (Ergun and Orning, 1949)

\[
\frac{D_c(t, z)}{d_p} = \frac{2}{3} \frac{1 - \phi_{sd}(t, z)}{\phi_{sd}(t, z)}
\]

\[
P(t) \frac{dP(t)}{dz} = -\frac{\mu Q_0 P_0}{\pi R_c^2 B_0(t, z)}
\]
Simplified clog model 1

Assumptions:
Particles deposited by interception

\[ \text{Clog } \phi_{sd,clog} = \phi_{sd,c} \]

\[ \phi_{sd,clog}(z) = \frac{V_p(z)}{\pi(R_c^2 - R_o^2)\Delta z} = \phi_{sd,c} \]

Clogging at \( R_o = 0 \)

Direction of flow

○ Nanoparticle

d_{p}

LD model

Cross-sectional view

Simplified model
**Simplified clog model 2**

Interception area

Fraction of particles within

Mass-balance

\[ X = \frac{C_0 \cdot 2\pi \Delta z}{R_o \cdot d_p} - \frac{R_o \cdot (d_p \cdot d_p)}{2} \]

\[ \int_{R_c}^{R_o} dR_o = - \frac{Q_0 C_0 \nu_p}{2\pi R_c^2 \phi_{sd,c}} \int_0^{t_{cl}} dt \Rightarrow t_{cl} = \frac{2R_c \phi_{sd,c}}{UC_0 \nu_p} \]
Estimation of clogging time

\[ t_{cl} = \frac{2R_c \phi_{sd,c}}{UC_0 v_p} \]

- \( R_c \): Capillary radius
- \( C_0 \): Aerosol concentration
- \( v_p \): Volume of single particle

Deviation at high Pe

Deviation at high Pe

\[ R^2 = 0.996 \]

Increasing Pe

\( Pe = 0.01 \rightarrow 10 \)
Clogging height

Growth of cone

Mass-balance: shaded area

\[ \pi (R_c^2 - R_o^2) \Delta z \cdot \phi_{sd,c} \]

Volume increase of cone

\[ \delta_{cl} = \frac{UC_0 v_p}{\phi_{sd,c}} t_{cl} \Rightarrow \]
Height of cone

\[ \delta_{dl} = 2R_c \ ? \]

\[ 2R_c \]

\[ Pe = 10 \]
Evolution of filtration efficiency

$\eta \rightarrow 1 \text{ at } t = t_{cl}$

Initially, more particles penetrate at high $Pe$

![Graph showing filtration efficiency over time with different Pe values and time markers at 130 s and 630 s.](image_url)
Nanoparticle filtration 2

- Formation of filter cake
  - Effect of varying filtration rate, filter geometry, particle/aggregate morphology on time for formation of filter cake (clogging time, $t_{cl}$) and cake solid volume fraction ($\phi_{sd,c}$)

- Optimization of filtration efficiency $\eta$
  Reduction of pressure-drop $\Delta P$
Outline

- Filtration theory
- Our approach
- Evolution of cake structure and pressure drop
- Conclusions